

Thermally induced mixing of water dominated interstellar ices

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Thermally induced mixing of water dominated interstellar ices

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Despite considerable attention in the literature being given to the desorption behaviour of smaller volatiles, the thermal properties of complex organics, such as ethanol ($\text{C}_2\text{H}_5\text{OH}$), which are predicted to be formed within interstellar ices, have yet to be characterized. With this in mind, reflection absorption infrared spectroscopy (RAIRS) and temperature programmed desorption (TPD) have been used to probe the adsorption and desorption of $\text{C}_2\text{H}_5\text{OH}$ deposited on top of water (H_2O) films of various thicknesses grown on highly oriented pyrolytic graphite (HOPG) at 98 K. Unlike many other molecules detected within interstellar ices, $\text{C}_2\text{H}_5\text{OH}$ has a comparable sublimation temperature to H_2O and therefore gives rise to a complicated desorption profile. RAIRS and TPD show that $\text{C}_2\text{H}_5\text{OH}$ is incorporated into the underlying ASW film during heating, due to a morphology change in both the $\text{C}_2\text{H}_5\text{OH}$ and H_2O ices. Desorption peaks assigned to $\text{C}_2\text{H}_5\text{OH}$ co-desorption with amorphous, crystalline (CI) and hexagonal H_2O -ice phases, in addition to $\text{C}_2\text{H}_5\text{OH}$ multilayer desorption are observed in the TPD. When $\text{C}_2\text{H}_5\text{OH}$ is deposited beneath ASW films, or is co-deposited as a mixture with H_2O , complete co-desorption is observed, providing further evidence of thermally induced mixing between the ices. $\text{C}_2\text{H}_5\text{OH}$ is also shown to modify the desorption of H_2O at the ASW-CI phase transition. This behaviour has not been previously reported for more commonly studied volatiles found within astrophysical ices. These results are consistent with astronomical observations, which suggest that gas-phase $\text{C}_2\text{H}_5\text{OH}$ is localized in hotter regions of the ISM, such as hot cores.

Introduction

Water (H_2O) is one of the most abundant molecular species observed in the interstellar medium (ISM) and is found in the form of interstellar ices frozen out on the surface of dust grains.¹ It has been well documented that interstellar dust grains play a pivotal role in the chemical and molecular evolutionary processes in the ISM.^{2–4} These H_2O ice covered grains open up reaction pathways to molecules and atoms that accrete on the grains that are not available in the gas-phase. The composition of interstellar ices is dominated by H_2O , which comprises up to 60–70% of the ice,^{5,6} and therefore plays a significant role in the chemistry of the ISM. Other major components within these ices include small saturated molecules such as methanol (CH_3OH) and carbon monoxide (CO). Furthermore, models predict that more complex saturated organics, such as ethanol ($\text{C}_2\text{H}_5\text{OH}$), which are formed *via* grain surface chemistry, are also present within these ices.^{7–10} It has been estimated that the $\text{C}_2\text{H}_5\text{OH}$ composition within these ices lies between 0.5% and 5% relative to H_2O .⁹ However, infrared space observatory (ISO) data suggests the upper limit of solid $\text{C}_2\text{H}_5\text{OH}$ to be 1.2% within these ices.¹¹

The evaporation of these chemically rich icy mantles from interstellar dust grains has been shown to play a key role in the chemistry of star-forming regions in the latter stages of development, known as hot molecular cores.^{12–16} Furthermore, the adsorption and desorption of astrophysical ices are also im-

portant in the sublimation and out-gassing processes of comets^{17–21} and in regions where shocks lead to sudden heating of the grains.^{22–24} Hence to facilitate accurate modelling of ISM processes, a detailed characterization of the adsorption and desorption of astrophysically relevant molecules from H_2O covered surfaces is essential. Despite considerable attention in the literature given to the thermal desorption of simple volatiles detected in H_2O -rich ices,^{25–33} the desorption of more complex saturated molecules, such as $\text{C}_2\text{H}_5\text{OH}$, has yet to be explored. We have therefore used reflection absorption infrared spectroscopy (RAIRS) and temperature programmed desorption (TPD) to investigate the adsorption and desorption of $\text{C}_2\text{H}_5\text{OH}$ from various thicknesses of amorphous solid water (ASW) grown on an underlying highly oriented pyrolytic graphite (HOPG) surface at 98 K. The exact composition of interstellar dust grains is still not accurately known and depends on the astrophysical environment. However, spectroscopic observations indicate that these grains are primarily composed of carbonaceous and silicate material.^{34,35} The carbon component of these grains is known to exist in various forms including graphite, diamond and amorphous carbon.³⁵ Hence the HOPG substrate used in this study can be considered a suitable dust grain analogue and has previously been used to investigate the formation of small molecules on model dust grain surfaces.^{36,37}

The interaction between H_2O ice films and astrophysically relevant gas-phase molecules, and the subsequent annealing of these model interstellar ices, has received considerable attention in the literature.^{25–33} Such processes are of particular importance to the ISM with regards to elucidating

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star-formation, in addition to determining the ice composition and thermal ageing of astrophysical bodies and out-gassing kinetics.²⁰ Several laboratory studies have demonstrated that the thermal desorption behaviour of molecules deposited on the surface of a H₂O film, or co-deposited as a mixture, are controlled by the morphology and desorption properties of the H₂O.^{25–32} H₂O ice is known to exist in a number of different phases, the physical properties of which depend on experimental factors including deposition temperature, deposition rate and the angular distribution of the impinging H₂O flux.^{38–41} Deposition temperatures below ~ 130 K lead to the formation of ASW and hence this is thought to be the dominant phase observed in the ISM.^{42,43} ASW exists in two distinct phases.³⁹ At low temperatures (~ 10 K) a high density amorphous form exists. This highly porous amorphous phase undergoes an irreversible phase transition to form a low density, less porous, amorphous phase over the temperature range from 38 K–68 K.⁴³ When heated above the glass transition temperature ($T_g = 136$ K), low density ASW undergoes a structural change, transforming into a metastable liquid prior to the formation of cubic crystalline ice (CI) at 160 K.^{44,45} At higher temperatures, CI converts to hexagonal ice.

There have been numerous TPD studies that have demonstrated the ability of ASW to trap astrophysically relevant molecules.^{25–29,31–33} Volatile species such as CO, argon, nitrogen, oxygen, methane and carbon dioxide, all give rise to two additional high temperature features in the TPD that are independent of the adsorbate. The first of these features is ascribed to an explosive desorption process corresponding to the ASW-CI phase transition, whereby trapped molecules that are incorporated into the H₂O bulk are released from the ice *via* the opening of connected pathways to the surface.⁴⁶ The second, higher temperature, feature is assigned to co-desorption with crystalline ice. Similar effects have also been observed for adsorbates dosed beneath thick ASW films.^{28,46}

In contrast, there have only been a few previous theoretical and experimental studies in the literature that have investigated binary layered C₂H₅OH/H₂O ices.^{47–50} The interaction of C₂H₅OH on ice surfaces has been investigated using density functional theory calculations⁴⁷ and molecular dynamics (MD) simulations,⁴⁸ with the adsorption of C₂H₅OH on the ice surface shown to occur *via* the formation of hydrogen bonds. Thermally induced mixing of layered binary amorphous C₂H₅OH and heavy water films has been reported by Souda and co-workers.⁴⁹ Using temperature programmed time-of-flight mass spectrometry, it was shown that C₂H₅OH was not incorporated into the underlying D₂O film at 15 K. However, subsequent annealing of the binary layers showed that thermally induced mixing occurred in two phases. The onset of mixing was observed at ~ 120 K, corresponding to a morphology change in the C₂H₅OH overlayer, leading to incomplete mixing. Complete mixing at the molecular level occurred between the layers above 140 K due to the increased mobility of the underlying D₂O film. The same authors reported almost identical behaviour for layered binary systems of CH₃OH and H₂O.^{51,52} Similarly, Wolff *et al.* observed thermally induced mixing when CH₃OH was deposited on ASW films adsorbed on an HOPG substrate at 97 K.⁵³ TPD showed that in addition to CH₃OH monolayer and multilayer

desorption, CH₃OH also exhibited a co-desorption feature with crystalline H₂O. However in this case, the mechanism was ascribed to the entrapment of CH₃OH at grain boundaries during the ASW-CI transition, rather than a complete mixing between the two films. A recent study performed by Bahr *et al.* investigated the interaction between CH₃OH and ASW adsorbed on polycrystalline Ag at 125 K.⁵⁴ Using a combination of metastable-impact-electron spectroscopy, RAIRS, TPD and MD calculations, it was shown that CH₃OH forms strong hydrogen bonds with the dangling OH bonds on the ASW surface upon adsorption. TPD data showed that when a submonolayer film of CH₃OH was deposited on top of ASW, it was not incorporated into the underlying film. However when the deposition sequence was reversed, the D₂O molecules became embedded in the underlying CH₃OH film.

In this paper we present the first detailed RAIRS and TPD study of C₂H₅OH desorption from H₂O-ice deposited on a model dust grain surface (HOPG) at 98 K. In addition, we also discuss the implications of the thermal desorption of the H₂O component of the ice, which is clearly affected by the presence of the C₂H₅OH ices. Modification of the H₂O thermal desorption profile has not previously been reported, despite numerous model interstellar ice investigations. In order to fully understand the complex thermal desorption processes of this binary system, reverse deposition experiments (*i.e.* various thicknesses of H₂O deposited on top of C₂H₅OH ices) and the adsorption of astrochemically relevant mixtures of C₂H₅OH:H₂O were also investigated. Although interstellar ices are expected to form complex mixtures, there is also evidence which suggests that H₂O-rich ices may undergo segregation as the temperature of the ice increases (> 80 K).⁵⁵ Hence, the investigation of layered binary ices, where C₂H₅OH is deposited on top of ASW, is relevant to the ISM and to cometary environments.^{55,56} Three different thicknesses of pre-deposited H₂O films are examined and are categorized as thin, medium and thick films, corresponding to H₂O exposures of 2, 10, and 50 L. It has been previously shown that H₂O does not wet the graphite surface and forms 2D (monolayer) and 3D (monolayer + bilayer) island clusters prior to forming a complete monolayer film.^{57,58} Hence, a 2 L exposure corresponds to a combination of H₂O clusters and bare patches of HOPG, a 10 L film corresponds to a saturated monolayer and a 50 L exposure leads to a thick amorphous film which undergoes a phase transition to a less porous phase (CI) prior to desorption. For clarity in the following discussion, the binary systems investigated in this study will be described as C₂H₅OH/H₂O(2 L), C₂H₅OH/H₂O(10 L) and C₂H₅OH/H₂O(50 L). This notation will also be extended to the reverse deposition systems, where H₂O is deposited on top of C₂H₅OH films, with the corresponding thickness of the C₂H₅OH film given in brackets.

Experimental

The apparatus used for the experiments reported here has been described elsewhere,⁵⁹ hence only a brief description will be given. Experiments were performed in an ultra high vacuum (UHV) apparatus with a base pressure of $\leq 2 \times 10^{-10}$ mbar. The HOPG sample was cleaned before each experiment by

annealing at 500 K in UHV for 3 minutes. Sample cleanliness was confirmed by the absence of any desorption during TPD experiments performed following no dosage. $\text{C}_2\text{H}_5\text{OH}$ (99.7–100% AnalaR BDH) and H_2O (distilled, deionized) were used to create the binary layered ices. Both were purified by repeated freeze-pump-thaw cycles. Gas mixtures were admitted into the chamber by the use of a high precision leak valve and deposited onto the HOPG substrate held at 98 K by backfilling the chamber. All exposures are measured in Langmuir (L), where $1 \text{ L} = 10^{-6} \text{ mbar s}$.

RAIR spectra were recorded using a Mattson Instruments RS1 Research Series Fourier transform infrared spectrometer coupled to a liquid nitrogen cooled MCT detector. All spectra were taken at a resolution of 4 cm^{-1} and are the result of the co-addition of 256 scans. For the annealed RAIRS experiments, the sample was held at a pre-determined temperature for 3 minutes before cooling back to the base temperature where a spectrum was recorded. TPD spectra were recorded with a Hiden Analytical HAL201 quadrupole mass spectrometer. The simultaneous desorption of mass 18 and mass 31, the major mass fragments of H_2O and $\text{C}_2\text{H}_5\text{OH}$, respectively, was recorded. All TPD spectra were recorded at a heating rate of $0.5 \pm 0.01 \text{ K s}^{-1}$.

Results and discussion

TPD data

H_2O desorption. Fig. 1 shows a series of TPD spectra for H_2O desorption from all three binary layered systems as a function of overlayer $\text{C}_2\text{H}_5\text{OH}$ exposure. TPD spectra arising from the $\text{C}_2\text{H}_5\text{OH}/\text{H}_2\text{O}(2 \text{ L})$ system following low $\text{C}_2\text{H}_5\text{OH}$ exposures see an immediate shift in desorption temperature

from 142 K for 2 L of pure H_2O to 145 K for $\text{C}_2\text{H}_5\text{OH}$ covered H_2O . The desorption temperature remains constant at 145 K for deposition of $\text{C}_2\text{H}_5\text{OH}$ up to exposures of 20 L. However, for $\text{C}_2\text{H}_5\text{OH}$ exposures above 20 L (corresponding to the onset of multilayer formation⁶⁰) a progressive upward shift in desorption temperature, and a gradual sharpening of the H_2O profile, is observed. By an $\text{C}_2\text{H}_5\text{OH}$ exposure of 300 L, the H_2O desorption profile has sharpened considerably and has a maximum desorption temperature of 154 K. As the exposure of H_2O remains constant for all of the TPD spectra shown in Fig. 1A, the area under the TPD traces should remain constant (within experimental error). However, for $\text{C}_2\text{H}_5\text{OH}$ exposures above 100 L, there is an increase in the integrated area under the H_2O TPD traces. This is discussed below.

The desorption of a 10 L film of H_2O covered by $\text{C}_2\text{H}_5\text{OH}$ (Fig. 1B), shows an immediate change upon $\text{C}_2\text{H}_5\text{OH}$ adsorption. At the lowest $\text{C}_2\text{H}_5\text{OH}$ exposures (5 L) the H_2O TPD trace sharpens compared to the pure H_2O ice and also exhibits a minor upward shift in desorption temperature from 151 K to 153 K. $\text{C}_2\text{H}_5\text{OH}$ exposures above 50 L also see the appearance of a high temperature shoulder on the main H_2O desorption peak at 156 K, in addition to an increase in desorption temperature of the main peak to 155 K at $\text{C}_2\text{H}_5\text{OH}$ exposures of 300 L. The high temperature feature becomes more prominent with increasing $\text{C}_2\text{H}_5\text{OH}$ exposure. As expected, the integrated area under the H_2O TPD traces remains constant at all $\text{C}_2\text{H}_5\text{OH}$ exposures.

In contrast to the $\text{C}_2\text{H}_5\text{OH}/\text{H}_2\text{O}(2 \text{ L})$ and $\text{C}_2\text{H}_5\text{OH}/\text{H}_2\text{O}(10 \text{ L})$ layered ices, H_2O desorption from the $\text{C}_2\text{H}_5\text{OH}/\text{H}_2\text{O}(50 \text{ L})$ system, shown in Fig. 1C, remains relatively unchanged as a function of $\text{C}_2\text{H}_5\text{OH}$ exposure, with only minor perturbations observed on the leading edge of the H_2O traces. As observed in

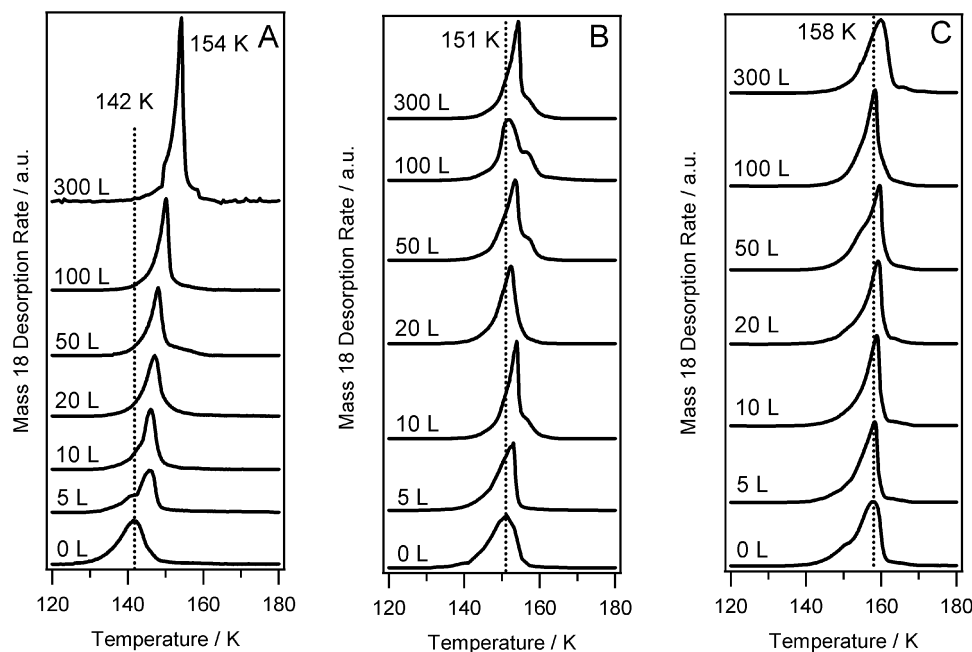


Fig. 1 TPD spectra showing the desorption of H_2O from layered binary $\text{C}_2\text{H}_5\text{OH}/\text{H}_2\text{O}$ ices for exposures of (A) 2 L, (B) 10 L and (C) 50 L H_2O grown on HOPG at 98 K. $\text{C}_2\text{H}_5\text{OH}$ exposures deposited onto the H_2O films are shown in the figure. TPD traces for pure H_2O ices with no $\text{C}_2\text{H}_5\text{OH}$ overlayer are also shown.

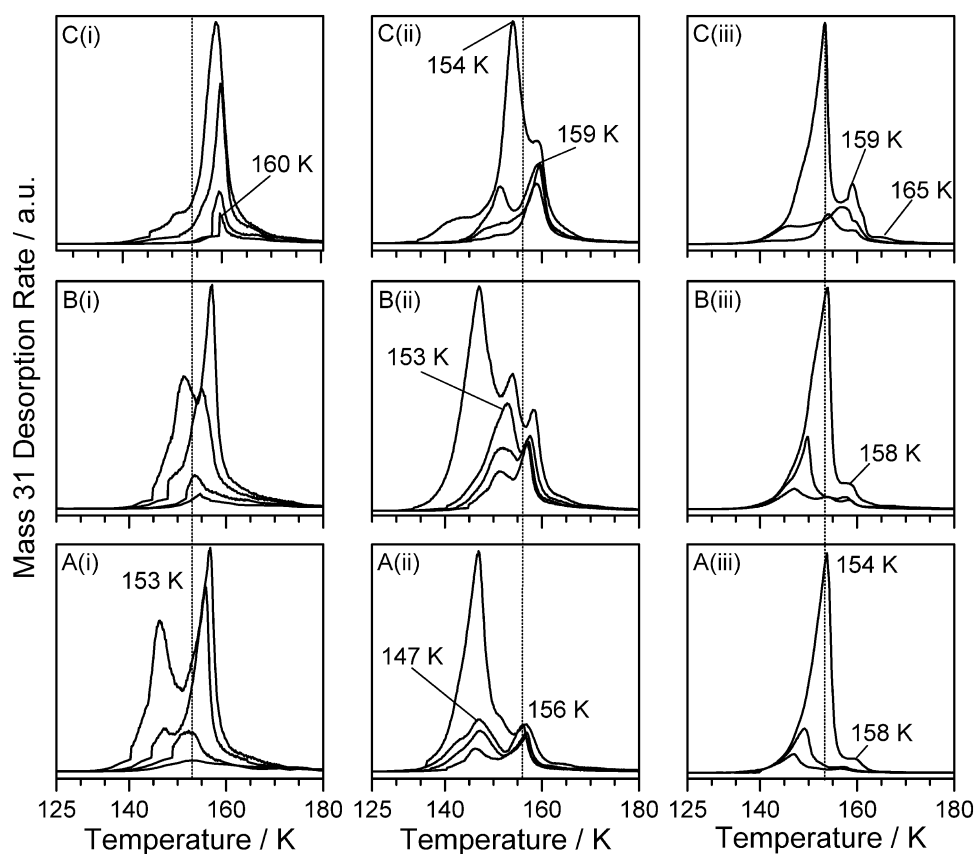


Fig. 2 TPD spectra for $\text{C}_2\text{H}_5\text{OH}$ adsorbed on underlying H_2O films resulting from exposures of (A) 2 L, (B) 10 L and (C) 50 L H_2O adsorbed on HOPG at 98 K. Panels on the left labelled (i) show low $\text{C}_2\text{H}_5\text{OH}$ exposures of 1, 2, 5 and 10 L. The central panels labelled (ii) show medium $\text{C}_2\text{H}_5\text{OH}$ exposures of 10, 15, 20 and 50 L. Panels on the right labelled (iii) show high $\text{C}_2\text{H}_5\text{OH}$ exposures of 50, 100 and 300 L.

the $\text{C}_2\text{H}_5\text{OH}/\text{H}_2\text{O}$ (10 L) system, the integrated area under the H_2O TPD spectra remains constant across the entire $\text{C}_2\text{H}_5\text{OH}$ exposure range. Closer comparison of the pure H_2O TPD trace with the H_2O TPD traces with an $\text{C}_2\text{H}_5\text{OH}$ overlayer, shows that the distinctive bump on the leading edge, ascribed to the ASW-CI phase transition, is not as prominent.

Fig. 1 clearly shows that H_2O desorption is impeded by the $\text{C}_2\text{H}_5\text{OH}$ overlayers, characterized by an upward shift in the maximum desorption temperature, in addition to the development of desorption features at higher temperatures for the $\text{C}_2\text{H}_5\text{OH}/\text{H}_2\text{O}$ (10 L) ices. The extent of these effects is dependent on the relative thicknesses of the two films, in addition to the difference between the respective H_2O and $\text{C}_2\text{H}_5\text{OH}$ film desorption temperatures. At low exposures (< 20 L), $\text{C}_2\text{H}_5\text{OH}$ has a tendency to form islands, hence the $\text{C}_2\text{H}_5\text{OH}$ overlayer does not significantly inhibit H_2O desorption. However, at exposures where $\text{C}_2\text{H}_5\text{OH}$ forms multilayers (≥ 50 L) the overlayer begins to impede H_2O desorption. Assuming that there is no mixing (or limited mixing) between the two layers, the sequential deposition of the films would prevent H_2O desorption prior to desorption of the $\text{C}_2\text{H}_5\text{OH}$ overlayer. The desorption temperatures for $\text{C}_2\text{H}_5\text{OH}$ when adsorbed on the H_2O ices range from 142 to 158 K for $\text{C}_2\text{H}_5\text{OH}$ exposures of 50 L–300 L. Since the H_2O desorption temperature increases with exposure (142 K for 2 L, 151 K for 10 L and 158 K for 50 L) the thinner H_2O films exhibit a greater deviation from the pure TPD spectrum. In the case of the 2 L

H_2O ice, the H_2O is held on the HOPG surface until ~ 12 K above its normal sublimation temperature. This results in an abrupt desorption from the surface that exceeds the pumping speed of the chamber, giving rise to an artificial enhancement of the measured TPD desorption trace. Similar explosive desorption has also been reported by Wolff *et al.* for layered binary films of $\text{CH}_3\text{OH}/\text{H}_2\text{O}$.⁵³ In contrast, 50 L H_2O films, which have a comparable desorption temperature to the $\text{C}_2\text{H}_5\text{OH}$ overlayer, remain relatively unchanged.

$\text{C}_2\text{H}_5\text{OH}$ desorption. Fig. 2 shows a series of $\text{C}_2\text{H}_5\text{OH}$ TPD spectra from pre-deposited H_2O films consisting of 2 L (Fig. 2A), 10 L (Fig. 2B) and 50 L (Fig. 2C) of H_2O grown on a HOPG surface exposed to increasing amounts of $\text{C}_2\text{H}_5\text{OH}$ at 98 K. Comparing the $\text{C}_2\text{H}_5\text{OH}$ TPD spectra for all three binary systems shown in Fig. 2, it is clear that the thickness of the underlying H_2O film has a significant effect on the $\text{C}_2\text{H}_5\text{OH}$ desorption profile. $\text{C}_2\text{H}_5\text{OH}$ desorption from the $\text{C}_2\text{H}_5\text{OH}/\text{H}_2\text{O}$ (2 L) and $\text{C}_2\text{H}_5\text{OH}/\text{H}_2\text{O}$ (10 L) ices exhibits three and four desorption species over the 300 L exposure range, respectively. TPD spectra for $\text{C}_2\text{H}_5\text{OH}$ deposited onto a 50 L thick ASW film are characterized by a contrasting and increasingly complex desorption behaviour compared to the thinner binary films. The TPD data shown in Fig. 2 will be initially described in a general manner, before providing a detailed discussion and full assignment of the $\text{C}_2\text{H}_5\text{OH}$ species desorbing from the model interstellar ices.

At low $\text{C}_2\text{H}_5\text{OH}$ exposures, each binary system is characterized by a single $\text{C}_2\text{H}_5\text{OH}$ desorption peak (153 K for the $\text{C}_2\text{H}_5\text{OH}/\text{H}_2\text{O}(2\text{ L})$ ice), which appears at higher temperatures with increasing thickness of the underlying H_2O ice. This peak saturates around 15 L for the $\text{C}_2\text{H}_5\text{OH}/\text{H}_2\text{O}(2\text{ L})$ and $\text{C}_2\text{H}_5\text{OH}/\text{H}_2\text{O}(10\text{ L})$ ices, desorbing at 156 and 159 K, respectively. The corresponding $\text{C}_2\text{H}_5\text{OH}$ desorption from the 50 L H_2O ice saturates at higher $\text{C}_2\text{H}_5\text{OH}$ exposures, desorbing at 159 K. A second, lower temperature, feature appears in the TPD spectrum at higher $\text{C}_2\text{H}_5\text{OH}$ exposures above 5 L. This feature desorbs at 147 and 153 K for $\text{C}_2\text{H}_5\text{OH}$ exposures of 20 L in the $\text{C}_2\text{H}_5\text{OH}/\text{H}_2\text{O}(2\text{ L})$ and $\text{C}_2\text{H}_5\text{OH}/\text{H}_2\text{O}(10\text{ L})$ binary ices, respectively. However, this peak appears at higher $\text{C}_2\text{H}_5\text{OH}$ exposures in the $\text{C}_2\text{H}_5\text{OH}/\text{H}_2\text{O}(50\text{ L})$ ice, around 15 L, desorbing at 154 K for $\text{C}_2\text{H}_5\text{OH}$ exposures of 50 L. Increasing the thickness of the underlying H_2O ice increases the dominance of this desorption feature up to $\text{C}_2\text{H}_5\text{OH}$ exposures of 50 L. $\text{C}_2\text{H}_5\text{OH}$ exposures of 50 L see the appearance of a third desorption peak in each TPD spectrum at $\sim 145\text{ K}$. This peak is characterized by a progressive upward shift in desorption temperature and intensity with increasing $\text{C}_2\text{H}_5\text{OH}$ exposure and dominates the TPD spectra for all three binary systems. Following an $\text{C}_2\text{H}_5\text{OH}$ exposure of 300 L this peak is observed at $\sim 154\text{ K}$. At high $\text{C}_2\text{H}_5\text{OH}$ exposures, the $\text{C}_2\text{H}_5\text{OH}/\text{H}_2\text{O}(2\text{ L})$ and $\text{C}_2\text{H}_5\text{OH}/\text{H}_2\text{O}(10\text{ L})$ layered ices exhibit very similar TPD spectra. An additional broad feature, common for $\text{C}_2\text{H}_5\text{OH}$ desorption from the 2 L and 10 L H_2O ices, appears on the high temperature side of the main desorption peak at around 158 K. In contrast, the $\text{C}_2\text{H}_5\text{OH}/\text{H}_2\text{O}(50\text{ L})$ system is characterized by a complex desorption profile in the high exposure regime.

Plotting the total integrated area under the TPD peaks shown in Fig. 2 as a function of $\text{C}_2\text{H}_5\text{OH}$ exposure (not shown) shows that the uptake of $\text{C}_2\text{H}_5\text{OH}$ is constant as a function of increasing exposure, suggesting that it forms physisorbed multilayers in all three binary systems, irrespective of the underlying H_2O film thickness. Furthermore, the integrated area of the TPD spectrum for every $\text{C}_2\text{H}_5\text{OH}$ exposure for each binary system is identical within experimental error. This suggests that the changes observed in the TPD profiles at the same $\text{C}_2\text{H}_5\text{OH}$ exposure are a result of the increased thickness of the H_2O layer and not a consequence of a change of sticking probability on bare patches of HOPG when compared to thick films of ASW.

The effects of increasing the underlying H_2O ice thickness on the desorption behaviour of $\text{C}_2\text{H}_5\text{OH}$ are more clearly illustrated in Fig. 3. In each case, TPD spectra for $\text{C}_2\text{H}_5\text{OH}$ adsorbed on bare HOPG have been included for comparison. $\text{C}_2\text{H}_5\text{OH}$ desorption from each of the three binary ices gives rise to a number of different species, with some features common to all three layered ice systems. To aid clarity in the following discussion, the assignments of each species, labelled in Fig. 3, will now be given. A detailed discussion of the origin of each assignment will be given later. Peak α is assigned to the desorption of an $\text{C}_2\text{H}_5\text{OH}$ monolayer, either from the HOPG surface or from the H_2O ice. This feature is observed for the $\text{C}_2\text{H}_5\text{OH}/\text{H}_2\text{O}(2\text{ L})$ and $\text{C}_2\text{H}_5\text{OH}/\text{H}_2\text{O}(10\text{ L})$ ices. A similar low exposure feature seen in the $\text{C}_2\text{H}_5\text{OH}/\text{H}_2\text{O}(50\text{ L})$ system is labelled α^* . Despite this feature exhibiting

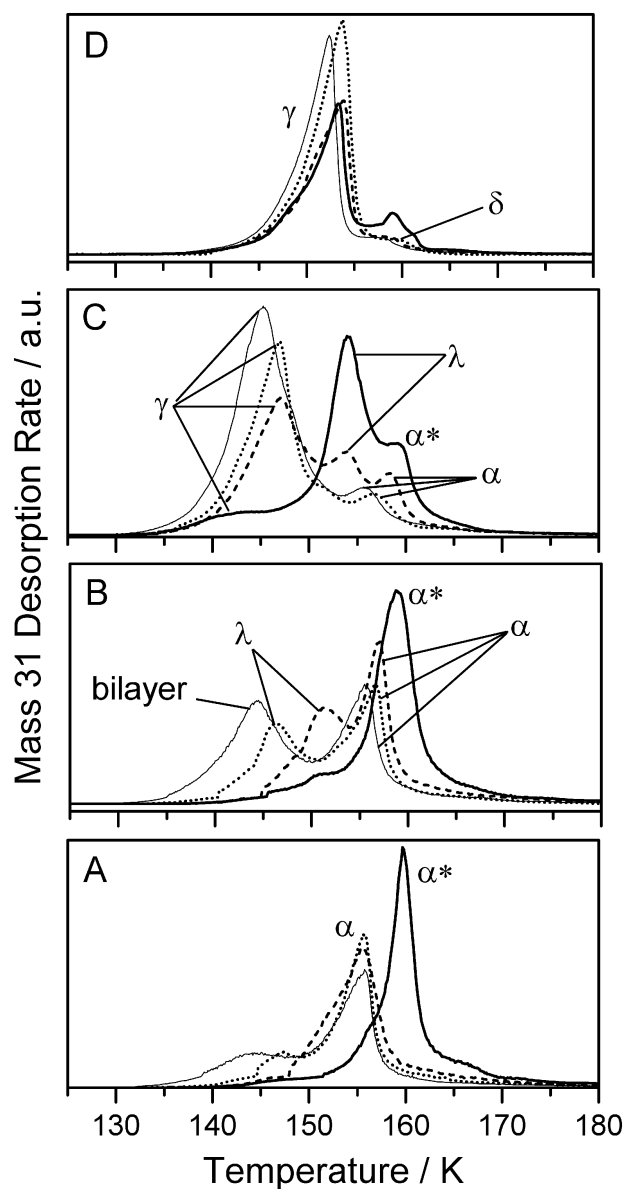


Fig. 3 Comparison of TPD spectra for $\text{C}_2\text{H}_5\text{OH}$ adsorbed on 2 L (dotted line), 10 L (dashed line) and 50 L (thick solid line) H_2O films. $\text{C}_2\text{H}_5\text{OH}$ desorption from a bare HOPG surface adsorbed at 98 K is also shown for comparison (thin solid line). $\text{C}_2\text{H}_5\text{OH}$ exposures are (A) 5 L, (B) 10 L, (C) 50 L and (D) 300 L, showing the changes in the $\text{C}_2\text{H}_5\text{OH}$ desorption features as a function of H_2O exposure.

behaviour that would initially suggest that it is of monolayer origin, closer inspection shows that this species arises from the co-desorption of $\text{C}_2\text{H}_5\text{OH}$ and CI due to thermally induced mixing between the $\text{C}_2\text{H}_5\text{OH}$ and H_2O layers (discussed later). Peaks γ and λ are assigned to $\text{C}_2\text{H}_5\text{OH}$ multilayer and trapped $\text{C}_2\text{H}_5\text{OH}$ released from ASW via a volcano desorption mechanism, respectively, and are common to all three layered ice systems. Peak δ is assigned to the desorption of crystalline $\text{C}_2\text{H}_5\text{OH}$.

The assignment of the TPD desorption features labelled δ and γ in Fig. 3C and D are made by comparing the TPD spectra arising from pure $\text{C}_2\text{H}_5\text{OH}$ ices⁶⁰ with those for $\text{C}_2\text{H}_5\text{OH}$ adsorbed on the H_2O ices. The broad high

temperature feature, labelled δ (Fig. 3D), which is common to the pure $\text{C}_2\text{H}_5\text{OH}$ ices and $\text{C}_2\text{H}_5\text{OH}$ desorption from 2 and 10 L H_2O ices, is assigned to the formation of crystalline $\text{C}_2\text{H}_5\text{OH}$ during the heating process. This feature has been previously characterized in a RAIRS and TPD study of pure $\text{C}_2\text{H}_5\text{OH}$ adsorption on HOPG.⁶⁰ The peak that dominates the $\text{C}_2\text{H}_5\text{OH}$ TPD spectrum for exposures above 50 L for all three binary systems, labelled γ (Fig. 3C and D), can be confidently assigned to the desorption of multilayer $\text{C}_2\text{H}_5\text{OH}$. Fig. 2 shows that the onset of multilayer growth is slower with increasing H_2O film thickness and this is more explicitly shown in Fig. 3C. This effect is attributed to the change in the relative surface area of the pre-deposited H_2O films adsorbed on HOPG, which increases with H_2O exposure. As a result, a greater exposure is required to saturate the $\text{C}_2\text{H}_5\text{OH}$ monolayer prior to formation of the multilayer as the H_2O film thickness increases. It is clear from Fig. 3C and D that the presence of H_2O on the HOPG surface modifies the desorption kinetics of multilayer $\text{C}_2\text{H}_5\text{OH}$ compared to the pure $\text{C}_2\text{H}_5\text{OH}$ ice. This is illustrated by an increase in the desorption temperature for peak γ for all three layered ices compared to the pure $\text{C}_2\text{H}_5\text{OH}$ multilayer. Furthermore, the leading edges of peak γ do not overlap with those for the pure $\text{C}_2\text{H}_5\text{OH}$ multilayer TPD spectrum, again indicating a change in the desorption kinetics. This change in the $\text{C}_2\text{H}_5\text{OH}$ multilayer desorption kinetics probably arises from thermally induced mixing between the two layers. Overlapping the $\text{C}_2\text{H}_5\text{OH}$ and H_2O TPD traces obtained in a single experiment for all three binary ices at $\text{C}_2\text{H}_5\text{OH}$ exposures where peak γ is present (not shown), shows that the $\text{C}_2\text{H}_5\text{OH}$ multilayer desorbs with the leading edge of the H_2O desorption. This implies a substantial diffusion of H_2O into the $\text{C}_2\text{H}_5\text{OH}$ overlayer and hence a modification of the H_2O TPD profile, as evidenced in Fig. 1. This is consistent with the thermally induced mixing between $\text{C}_2\text{H}_5\text{OH}$ and H_2O layers reported previously.⁴⁹

Assignment of the three low temperature features for the binary ices labelled α , α^* and λ in Fig. 3A, B and C is also made by comparison with the pure $\text{C}_2\text{H}_5\text{OH}$ TPD spectra as well as by overlapping the respective $\text{C}_2\text{H}_5\text{OH}$ and H_2O TPD spectra obtained for a single experiment. The TPD traces in Fig. 3 show that $\text{C}_2\text{H}_5\text{OH}$ desorption from the $\text{C}_2\text{H}_5\text{OH}/\text{H}_2\text{O}(2\text{ L})$ layered ices exhibits very similar behaviour to that observed for the pure $\text{C}_2\text{H}_5\text{OH}$ films. Hence peak α can be confidently assigned to the desorption of the $\text{C}_2\text{H}_5\text{OH}$ monolayer. This assignment also holds for the $\text{C}_2\text{H}_5\text{OH}/\text{H}_2\text{O}(10\text{ L})$ layered ices. The broadening of the monolayer TPD profile, in addition to the increase in desorption temperature, is consistent with the increased surface area and heterogeneity of the thicker H_2O films.

The TPD data shown in Fig. 2C(i) and 3A clearly show that peak α^* for the $\text{C}_2\text{H}_5\text{OH}/\text{H}_2\text{O}(50\text{ L})$ system exhibits different desorption behaviour to the corresponding monolayer peak observed for the thinner H_2O ices. The monolayer peak is characterized by a small increase in desorption temperature for $\text{C}_2\text{H}_5\text{OH}$ exposures ranging from 1 L to 10 L for both the $\text{C}_2\text{H}_5\text{OH}/\text{H}_2\text{O}(2\text{ L})$ (Fig. 2A(i)) and $\text{C}_2\text{H}_5\text{OH}/\text{H}_2\text{O}(10\text{ L})$ (Fig. 2B(i)) binary ices. In contrast, Fig. 2C(i) shows that the corresponding feature in the $\text{C}_2\text{H}_5\text{OH}/\text{H}_2\text{O}(50\text{ L})$ ice exhibits

a small decrease in temperature from 160 K to 159 K over a similar exposure range. In addition, overlapping TPD spectra for a 5 L $\text{C}_2\text{H}_5\text{OH}$ exposure adsorbed on varying thicknesses of H_2O (Fig. 3A) shows that peak α^* in the 50 L binary ice clearly desorbs at a higher temperature, whereas $\text{C}_2\text{H}_5\text{OH}$ desorption from the thinner films closely resembles $\text{C}_2\text{H}_5\text{OH}$ desorption from bare HOPG. This pattern is consistent for low $\text{C}_2\text{H}_5\text{OH}$ exposures ranging from 1 to 5 L. The contrasting nature of peak α^* in the $\text{C}_2\text{H}_5\text{OH}/\text{H}_2\text{O}(50\text{ L})$ ice is further confirmed in Fig. 4, which overlaps the corresponding $\text{C}_2\text{H}_5\text{OH}$ and H_2O TPD spectra obtained from a 20 L $\text{C}_2\text{H}_5\text{OH}$ exposure deposited on top of H_2O films of varying thicknesses. Fig. 4A and B clearly show that $\text{C}_2\text{H}_5\text{OH}$ desorption assigned to peak α occurs after H_2O desorption is complete for both the $\text{C}_2\text{H}_5\text{OH}/\text{H}_2\text{O}(2\text{ L})$ and $\text{C}_2\text{H}_5\text{OH}/\text{H}_2\text{O}(10\text{ L})$ ices. However, the $\text{C}_2\text{H}_5\text{OH}/\text{H}_2\text{O}(50\text{ L})$ system (Fig. 4C) shows that peak α^* co-desorbs with multilayer H_2O . This behaviour is consistent for all $\text{C}_2\text{H}_5\text{OH}$ exposures in all ice configurations where peak α^* is visible in the TPD spectrum. The simultaneous desorption of $\text{C}_2\text{H}_5\text{OH}$ with H_2O in the $\text{C}_2\text{H}_5\text{OH}/\text{H}_2\text{O}(50\text{ L})$ binary system could either indicate co-desorption from the ASW surface or be as a result of thermally induced mixing between the two layers. Data for reverse deposition and co-deposition of H_2O and $\text{C}_2\text{H}_5\text{OH}$ (shown later) suggest the latter assignment is the more likely and that peak α^* is due to thermally induced mixing between the $\text{C}_2\text{H}_5\text{OH}$ and H_2O layers.

Fig. 3B shows that peak λ desorbs at higher temperatures for all three binary ices when compared to the corresponding peak assigned to the $\text{C}_2\text{H}_5\text{OH}$ bilayer observed in the pure $\text{C}_2\text{H}_5\text{OH}$ ice.⁶⁰ Furthermore, peak λ becomes increasingly prominent in the TPD spectrum for the thicker H_2O ices, particularly at higher $\text{C}_2\text{H}_5\text{OH}$ exposures (Fig. 3C). The contrasting behaviour of peak λ compared to the bilayer in the pure $\text{C}_2\text{H}_5\text{OH}$ TPD spectrum (which is characterized by a peak growing into the TPD spectrum at 144 K at an $\text{C}_2\text{H}_5\text{OH}$ exposure 5 L, before becoming obscured by multilayer growth at 25 L⁶⁰) clearly shows that this feature is not due to the formation of an $\text{C}_2\text{H}_5\text{OH}$ bilayer. Instead this peak must arise from an interaction between $\text{C}_2\text{H}_5\text{OH}$ and H_2O adsorbed on the HOPG surface. Fig. 4C shows that peak λ desorbs with the leading edge of the H_2O desorption. This correlation is observed for $\text{C}_2\text{H}_5\text{OH}$ exposures ranging from 10 L to 50 L. The bump on the leading edge of the H_2O profile corresponds to the ASW-CI phase transition for pure H_2O ices.^{58,61,62} Hence, λ is assigned to a volcano desorption feature⁴⁶ whereby $\text{C}_2\text{H}_5\text{OH}$ molecules that have become trapped in the H_2O bulk, as a result of heat induced mixing between the two layers, are released from the H_2O lattice *via* the opening of connected desorption pathways in the H_2O ice prior to crystallization. A similar volcano peak has also been observed for the desorption of CH_3OH from $\text{CH}_3\text{OH}/\text{H}_2\text{O}$ layered ices adsorbed on HOPG at 97 K.⁵³

The TPD spectra for both $\text{C}_2\text{H}_5\text{OH}$ and H_2O shown in Fig. 4 provide evidence that $\text{C}_2\text{H}_5\text{OH}$ thermally mixes with the H_2O overlayer prior to desorption. The existence of a trapped $\text{C}_2\text{H}_5\text{OH}$ feature in the TPD spectra that is released, either by co-desorption with H_2O or *via* a change in morphology of the H_2O film, can only be as a result of intermixing between the

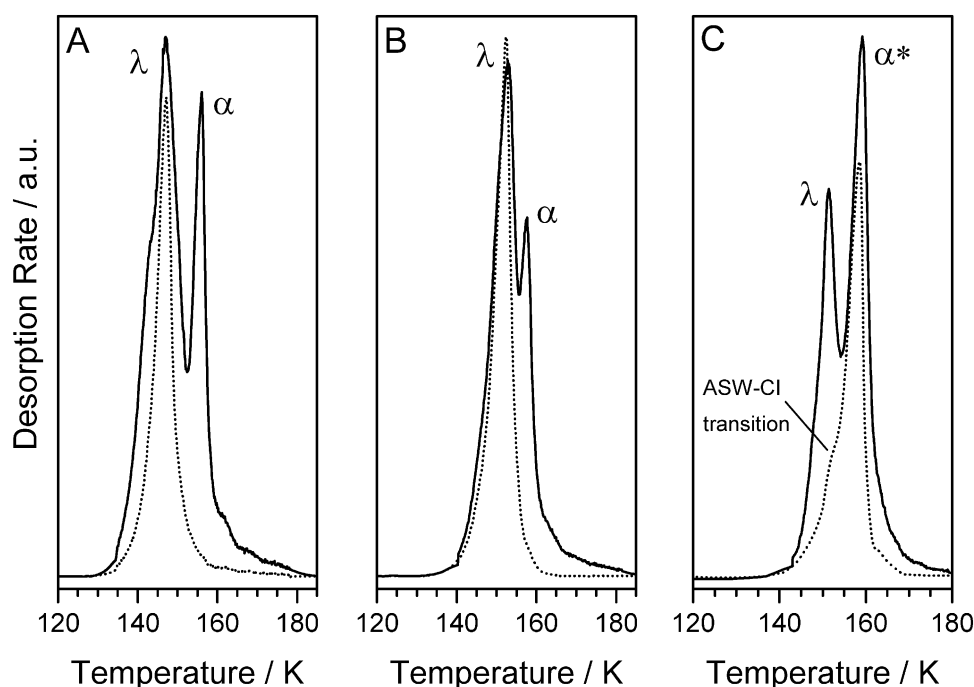


Fig. 4 TPD spectra overlaying desorption traces from a 20 L exposure of $\text{C}_2\text{H}_5\text{OH}$ (solid lines) on top of (A) 2 L, (B) 10 L and (C) 50 L thick H_2O ices (dotted lines) adsorbed on HOPG at 98 K. The H_2O TPD spectrum in each case has been scaled for clarity.

two layers during annealing. The greater prominence of the trapped feature in the TPD spectra for the 10 L and 50 L systems (Fig. 3C) is attributed to the increased thickness of the underlying H_2O film, which has a greater capacity to trap higher volumes of $\text{C}_2\text{H}_5\text{OH}$ during the structural rearrangement of both ice layers. However, the growth of an $\text{C}_2\text{H}_5\text{OH}$ multilayer in the TPD, for all H_2O ice thicknesses, shows that not all of the $\text{C}_2\text{H}_5\text{OH}$ is incorporated into the H_2O ice. This mixing also explains the appearance of the high temperature feature observed for very high exposures of $\text{C}_2\text{H}_5\text{OH}$ (≥ 100 L) in the $\text{C}_2\text{H}_5\text{OH}/\text{H}_2\text{O}$ (50 L) system (Fig. 2C(iii)). The high temperature shoulder mirrors the desorption of the broad low intensity H_2O peak at 165 K. This feature can therefore be assigned to co-desorption of $\text{C}_2\text{H}_5\text{OH}$ with hexagonal H_2O , which has also been observed for the co-deposited $\text{C}_2\text{H}_5\text{OH}:\text{H}_2\text{O}$ system.⁶³

In order to fully explore the dynamics of $\text{C}_2\text{H}_5\text{OH}$ desorption and the thermally induced mixing process further, the deposition sequence was reversed, with increasing exposures of H_2O deposited on top of a saturated $\text{C}_2\text{H}_5\text{OH}$ monolayer film (15 L) and multilayer film (50 L) grown on HOPG at 98 K (Fig. 5). Thermal processing and re-adsorption cycles, experienced in astrophysical environments as dust grains enter warm and cooler regions of the ISM, suggest that it is highly likely that segregated layers of $\text{C}_2\text{H}_5\text{OH}$ ice could be formed under thick layers of H_2O -ice.⁵⁵ Hence reversing the deposition sequence of the binary ices is important to obtain a better understanding of the thermal processes within the ISM. It is clear from the TPD traces shown in Fig. 5 that intermixing between the two layers occurs as expected, and common trends are observed when compared to the $\text{C}_2\text{H}_5\text{OH}/\text{H}_2\text{O}$ (50 L) system. Increasing the H_2O overlayer thickness sees a significant change in the $\text{C}_2\text{H}_5\text{OH}$ desorption profile. For the $\text{H}_2\text{O}/$

$\text{C}_2\text{H}_5\text{OH}$ (15 L) films (Fig. 5A(i)), the two well defined peaks seen for the pure $\text{C}_2\text{H}_5\text{OH}$ ice are characterized by an upward shift in temperature and develop into a single feature with a low temperature shoulder on the leading edge with increasing H_2O thickness. The desorption temperature of this feature is coincident with crystalline H_2O desorption at 160 K (Fig. 5A(ii)). Furthermore, the corresponding H_2O TPD spectra remain relatively unchanged for overlayer exposures up to 50 L (Fig. 5A(ii)). However, H_2O exposures of 100 L give rise to a sharpened CI desorption peak at 160 K with a low temperature shoulder at 155 K. The changes observed in both the $\text{C}_2\text{H}_5\text{OH}$ and H_2O TPD traces for the $\text{H}_2\text{O}/\text{C}_2\text{H}_5\text{OH}$ (50 L) system (Fig. 5B) are more marked, but exhibit similar trends to those shown for the $\text{H}_2\text{O}/\text{C}_2\text{H}_5\text{OH}$ (15 L) system. The two broad $\text{C}_2\text{H}_5\text{OH}$ desorption features observed in the pure $\text{C}_2\text{H}_5\text{OH}$ ice resolve into two sharp well defined peaks, exhibiting increased desorption temperatures of 157 and 160 K, respectively. The H_2O TPD traces for 50 and 100 L H_2O films are also characterized by a sharpening of the CI desorption peak, in addition to the formation of a low temperature peak on the leading edge, which appears on the 100 L H_2O spectrum at 157 K.

The TPD data in Fig. 5 show that $\text{C}_2\text{H}_5\text{OH}$ behaves differently to other astrophysically relevant molecules when deposited underneath a thick ASW film,^{28,64} underlining the value of investigating more complex organic molecules that are predicted to form within interstellar ices. Previous studies have shown that some small molecules, such as CO ,⁶⁴ are able to diffuse through the H_2O ice, giving rise to a low temperature feature dependent on the adsorbate sublimation temperature, in addition to desorption features corresponding to the ASW-CI transition and co-desorption with CI. For the thick H_2O overlayers, Fig. 5 shows that there is complete co-desorption

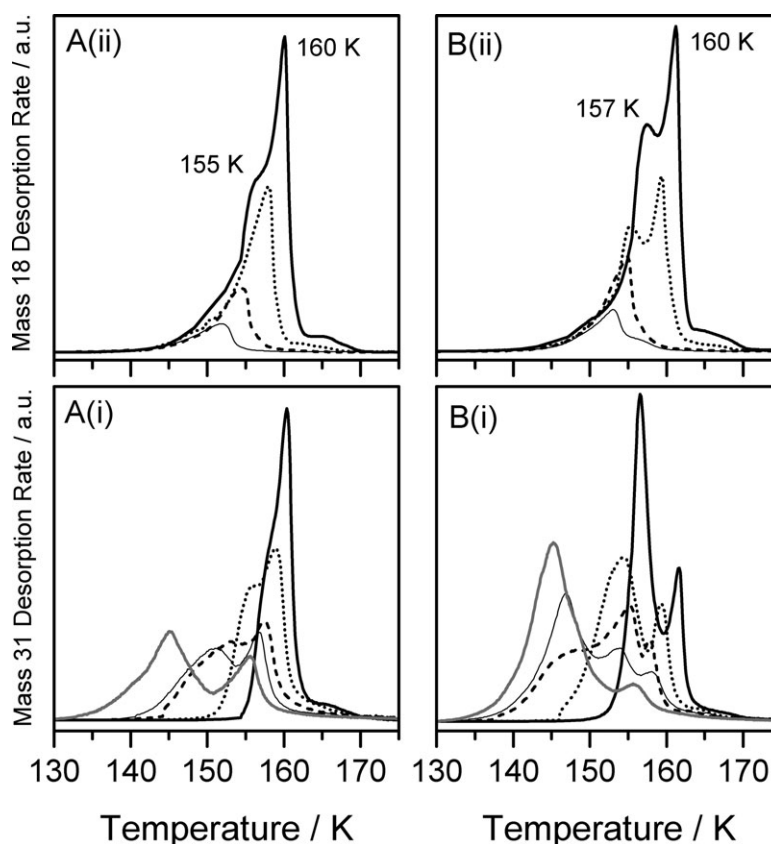


Fig. 5 TPD spectra following increasing exposures of H₂O deposited onto pre-existing C₂H₅OH films adsorbed on HOPG at 98 K. Fig. (A) shows (i) C₂H₅OH and (ii) H₂O desorption traces from a 15 L C₂H₅OH film. (B) shows the corresponding (i) C₂H₅OH and (ii) H₂O TPD arising from a 50 L C₂H₅OH film. In each case the H₂O exposures were 10 (thin solid lines), 20 (dashed lines), 50 (dotted lines) and 100 L (thick solid lines). The corresponding pure C₂H₅OH TPD traces (grey solid lines) are included for comparison.

and no evidence of desorption corresponding to the sublimation temperature of multilayer C₂H₅OH. This is more clearly seen in Fig. 6, which compares TPD spectra for 50 L C₂H₅OH exposures from both layered ice configurations and pure C₂H₅OH ices. Clearly, the diffusion process between the layers that occurs during heating leads to intermixing, whereby the H₂O/C₂H₅OH systems give similar TPD features to those observed for the C₂H₅OH/H₂O(50 L) ices. Hence, the C₂H₅OH feature desorbing at 157 K in the H₂O/C₂H₅OH(50 L) ices (Fig. 5B(i)), is coincident with the ASW-CI phase transition in the H₂O film and is therefore assigned to peak λ as seen for the C₂H₅OH/H₂O layered ices.

Fig. 6 also shows that peak α^* in the C₂H₅OH/H₂O(50 L) system overlaps with the high temperature feature observed when the deposition sequence is reversed. The correlation between the two peaks again suggests that peak α^* is not a surface co-desorption feature, but occurs as a result of thermally induced mixing between the layers. Confirmation of thermally induced mixing between the layers is also shown in the inset to Fig. 6, which compares C₂H₅OH desorption from the C₂H₅OH/H₂O(50 L) binary ice with an C₂H₅OH TPD trace obtained from the co-deposition of a mixture of C₂H₅OH:H₂O (1:5 ratio). The resulting TPD spectra were characterized by H₂O desorption that followed identical behaviour to pure H₂O desorption, coupled with co-desorption of C₂H₅OH from the ice. The C₂H₅OH TPD spectra shown in

the inset to Fig. 6 clearly show that a 10 L exposure of C₂H₅OH deposited on a 50 L H₂O film exhibits almost identical desorption behaviour to an equivalent concentration of C₂H₅OH co-deposited with H₂O. Furthermore, when overlapping the C₂H₅OH TPD spectrum from the mixtures shown in the inset to Fig. 6 with the TPD traces in the main figure, it is clear that the C₂H₅OH feature from the ice mixtures has an identical desorption temperature to peak α^* for the C₂H₅OH/H₂O(50 L) ice and the corresponding peak observed for the H₂O/C₂H₅OH(50 L) system. Hence peak α^* in the C₂H₅OH/H₂O(50 L) ice is assigned to the thermally induced mixing between the two layers. As already noted, this has previously been observed during the annealing of C₂H₅OH/D₂O binary ices.⁴⁹

Previous studies that have focussed on the desorption of smaller molecules in interstellar ices have not reported any significant change to the H₂O desorption profile during thermal desorption experiments.²⁵ However, Fig. 5 clearly shows that when H₂O is deposited on top of the C₂H₅OH ice, the desorption profile is perturbed when compared to that of pure H₂O (Fig. 1C). The characteristic bump on the leading edge of the H₂O desorption profile, assigned to the ASW-CI phase transition, becomes more pronounced for the thicker H₂O films. The modification to the H₂O desorption profile suggests that the presence of C₂H₅OH within the thermally processed ice can disrupt H₂O desorption to some extent, especially if the

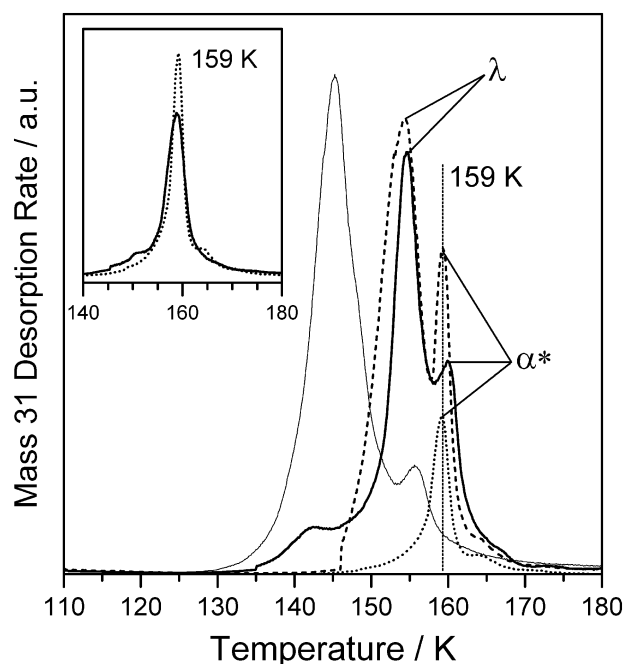


Fig. 6 TPD spectra comparing the desorption of 50 L $\text{C}_2\text{H}_5\text{OH}$ from different ice configurations: $\text{C}_2\text{H}_5\text{OH}$ adsorbed on top of a 50 L H_2O film (thick solid line), $\text{C}_2\text{H}_5\text{OH}$ dosed underneath a 50 L H_2O film (dashed line) and $\text{C}_2\text{H}_5\text{OH}$ desorption from a bare HOPG surface (thin solid line). The dotted line shows $\text{C}_2\text{H}_5\text{OH}$ desorption from a co-deposited $\text{C}_2\text{H}_5\text{OH}:\text{H}_2\text{O}$ mixture (1:5 ratio) and corresponds to an equivalent exposure of 10 L of pure $\text{C}_2\text{H}_5\text{OH}$. The inset compares the TPD spectrum from a co-deposited $\text{C}_2\text{H}_5\text{OH}:\text{H}_2\text{O}$ mixture (dotted line) shown in the main figure to $\text{C}_2\text{H}_5\text{OH}$ desorption from 10 L $\text{C}_2\text{H}_5\text{OH}$ deposited on a 50 L H_2O film (solid line). In each case the substrate temperature was 98 K.

$\text{C}_2\text{H}_5\text{OH}$ multilayer channel is not accessible (as in the case for the $\text{C}_2\text{H}_5\text{OH}/\text{H}_2\text{O}$ ices). This effect has not been observed for smaller volatiles, which have been shown to diffuse through the ASW ice.

RAIRS data

$\text{C}_2\text{H}_5\text{OH}$ adsorption on ASW. To investigate the interaction of $\text{C}_2\text{H}_5\text{OH}$ on the ASW surface further, a series of RAIRS experiments were also performed. Fig. 7 shows a RAIR spectrum for a 300 L exposure of $\text{C}_2\text{H}_5\text{OH}$ deposited on top of an existing 50 L H_2O ice film adsorbed on HOPG at 98 K. Fig. 7 also shows RAIR spectra for pure $\text{C}_2\text{H}_5\text{OH}$ (300 L) and pure H_2O (50 L) ices adsorbed on bare HOPG at 98 K. The adsorption, desorption, and a full assignment of the infrared bands for both pure ices have been reported previously.^{58,60} The broad band at 3396 cm^{-1} , with a low frequency shoulder at 3307 cm^{-1} , is assigned to the $\nu(\text{OH})$ vibrational mode in the H_2O RAIR spectrum and is characteristic of the formation of ASW.⁵⁸

It is clear that the vibrational bands and corresponding frequencies of the $\text{C}_2\text{H}_5\text{OH}/\text{H}_2\text{O}$ (50 L) layered ice (with the exception of the broad infrared feature in the $3600\text{--}3000\text{ cm}^{-1}$ region of the spectrum) are almost identical to those seen for the pure $\text{C}_2\text{H}_5\text{OH}$ ice adsorbed on HOPG.⁶⁰ Hence the infrared bands observed in the binary ice can be assigned

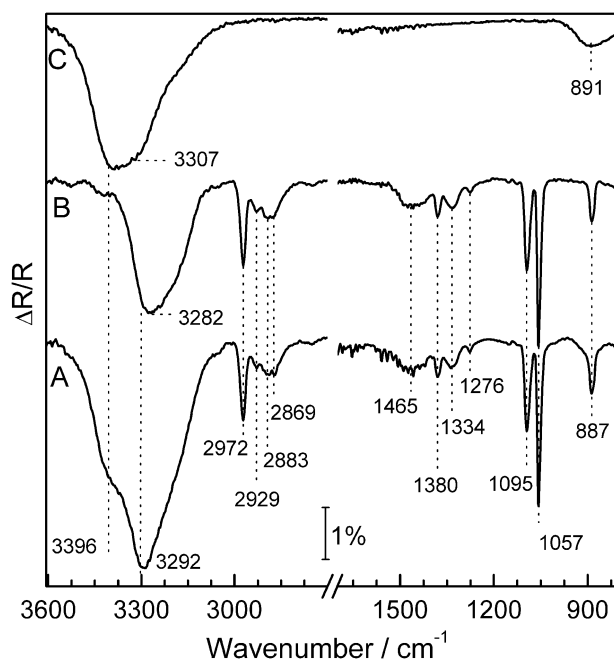


Fig. 7 Trace A shows the RAIR spectrum for a 300 L exposure of $\text{C}_2\text{H}_5\text{OH}$ deposited on top of a 50 L H_2O film adsorbed on HOPG at 98 K. Traces B and C show RAIR spectra for pure $\text{C}_2\text{H}_5\text{OH}$ (300 L) and pure H_2O (50 L), respectively, adsorbed on HOPG at 98 K. The region between 2700 cm^{-1} and 1700 cm^{-1} , which contains no infrared bands, has been omitted for clarity.

directly to the vibrational bands seen for $\text{C}_2\text{H}_5\text{OH}$ adsorption on HOPG. The similarity between the RAIR spectra for $\text{C}_2\text{H}_5\text{OH}$ adsorption on HOPG and $\text{C}_2\text{H}_5\text{OH}$ adsorbed on an ASW film implies that the ices retain a layered morphology upon adsorption at 98 K. This is further evidenced by the fact that the complex $\nu(\text{OH})$ stretching mode in the $3600\text{--}3000\text{ cm}^{-1}$ region of the spectrum for the $\text{C}_2\text{H}_5\text{OH}/\text{H}_2\text{O}$ (50 L) ice can be accurately modelled by a summation of the pure $\text{C}_2\text{H}_5\text{OH}$ and H_2O components. The combination of the H_2O and $\text{C}_2\text{H}_5\text{OH}$ $\nu(\text{OH})$ frequencies leads to an upward shift of the $\nu(\text{OH})$ band from 3282 cm^{-1} for the pure $\text{C}_2\text{H}_5\text{OH}$ ice to 3292 cm^{-1} for the $\text{C}_2\text{H}_5\text{OH}/\text{H}_2\text{O}$ (50 L) layered system at 98 K (Fig. 7).

Further similarities between $\text{C}_2\text{H}_5\text{OH}$ adsorption on bare HOPG and on the ASW ice are observed during stepwise adsorption. Once the infrared bands have grown into the spectrum, increasing the $\text{C}_2\text{H}_5\text{OH}$ exposure up to 300 L sees a corresponding increase in intensity of all bands with no associated spectral shifts. The exception to this is a noticeable broadening of the $\nu(\text{OH})$ band on the low frequency side for exposures above 50 L, due to the increasing contribution of the $\text{C}_2\text{H}_5\text{OH}$ $\nu(\text{OH})$ band (observed at 3280 cm^{-1} in the pure ice). Furthermore, none of the bands saturate with increasing coverage. These observations suggest that $\text{C}_2\text{H}_5\text{OH}$ forms physisorbed multilayers on ASW, as observed for $\text{C}_2\text{H}_5\text{OH}$ adsorption on bare HOPG.⁶⁰ This is also in agreement with the uptake curves determined from the TPD spectra shown in Fig. 2.

There are, however, some differences with regards to the growth of the observed vibrational bands between the pure

and ASW systems during $\text{C}_2\text{H}_5\text{OH}$ adsorption. The appearance of the band at 1382 cm^{-1} , assigned to the $\delta_s(\text{CH}_3)$ deformation, is delayed on ASW to an exposure of 50 L rather than appearing at 5 L, as on the bare HOPG surface.⁶⁰ In addition, the $\nu(\text{OH})$ band appears immediately when $\text{C}_2\text{H}_5\text{OH}$ is adsorbed on ASW at the lowest exposures and is characterized by a broadening of the existing $\nu(\text{OH})$ band arising from the ASW film. For $\text{C}_2\text{H}_5\text{OH}$ adsorbed on bare HOPG, the $\nu(\text{OH})$ band is not observed until an exposure of 10–15 L of $\text{C}_2\text{H}_5\text{OH}$, which implies that the OH group is almost parallel to the surface. This suggests that at low exposures, $\text{C}_2\text{H}_5\text{OH}$ adopts a different orientation on the ASW surface compared to adsorption on HOPG. This is expected, since ASW has dangling OH bonds at the surface, which would facilitate the formation of hydrogen bonds.^{65,66} Theoretical simulations have shown that $\text{C}_2\text{H}_5\text{OH}$ is adsorbed on the $\text{I}_h(0001)$ ice surface *via* the formation of hydrogen bonds.^{47,48} Furthermore, a similar orientation change, with the hydroxyl group of CH_3OH pointing towards the dangling bonds of an ASW film, has been previously reported for submonolayer CH_3OH adsorbed on ASW films at 125 K and was attributed to the formation of hydrogen bonds.⁵⁴ However, the exact nature of the hydrogen bonding interaction between $\text{C}_2\text{H}_5\text{OH}$ and H_2O cannot be confirmed in this study due to the inherently weaker infrared signal reflected from HOPG compared to metal surfaces. Previous studies of pure H_2O ices adsorbed on HOPG were also unable to detect the weak OH dangling bond signal.⁵⁸

Annealing the $\text{C}_2\text{H}_5\text{OH}/\text{H}_2\text{O}$ ices. The desorption behaviour of the binary system was investigated by performing a series of annealing experiments in order to identify the onset of thermally induced mixing observed in the TPD. Fig. 8A shows RAIR spectra for the $\nu(\text{OH})$ band following the annealing of 300 L $\text{C}_2\text{H}_5\text{OH}$ adsorbed on 50 L of H_2O on HOPG at 98 K. Annealing to 124 K sees the distinct high frequency shoulder

at 3396 cm^{-1} smoothing out to form a single broad band at 3292 cm^{-1} with a reduced intensity. Further heating sees a continued decrease in band intensity, accompanied by a 50 cm^{-1} downshift to 3242 cm^{-1} by 150 K. By 159 K the signal has disappeared from the spectrum, indicating that both $\text{C}_2\text{H}_5\text{OH}$ and H_2O have desorbed from the HOPG surface. The remaining infrared bands in the RAIR spectrum are characterized by a gradual decrease in intensity as the annealing temperature is increased, with no associated shifts or band splitting. All features have disappeared from the spectrum by 159 K, indicating that $\text{C}_2\text{H}_5\text{OH}$ has desorbed from the surface.

The changes to the $\nu(\text{OH})$ profile during annealing are in complete contrast to those observed for both pure $\text{C}_2\text{H}_5\text{OH}$ (Fig. 8B) and pure H_2O ices. Annealing pure $\text{C}_2\text{H}_5\text{OH}$ ices to 122 K gives rise to a sharpening of the $\nu(\text{OH})$ vibrational mode coupled with an increase in band amplitude. Annealing to 140 K sees this band split into three different bands prior to desorption at 162 K.⁶⁰ Similar $\nu(\text{OH})$ band splitting is also observed for the annealing of pure H_2O to 145 K.⁵⁸ In each case, these observations were ascribed to a change in morphology of the pure ices from an amorphous phase to a crystalline phase. It is evident from the data shown in Fig. 8 that annealing the binary ices does not lead to the crystallization of the $\text{C}_2\text{H}_5\text{OH}$ ice. The RAIRS data in Fig. 8A also suggest that crystallization of the H_2O film is inhibited by the annealing process. However, the H_2O TPD data for the $\text{C}_2\text{H}_5\text{OH}/\text{H}_2\text{O}$ (50 L) ices (Fig. 1C) are characterized by a bump on the leading edge of the main H_2O desorption peak caused by ASW crystallization.^{58,61,62} Hence, it is likely that the ASW-CI phase transition in the RAIRS is obscured by the broadening of the $\text{C}_2\text{H}_5\text{OH}$ $\nu(\text{OH})$ vibrational band.

Similar broadening of the $\nu(\text{OH})$ vibrational band during the annealing of binary layered CH_3OH and $\text{C}_2\text{H}_5\text{OH}$ systems has been reported by Ayotte *et al.*⁶⁷ and was assigned to thermally induced mixing between the two layers. The observations for our $\text{C}_2\text{H}_5\text{OH}/\text{H}_2\text{O}$ (50 L) system (Fig. 8A) can also

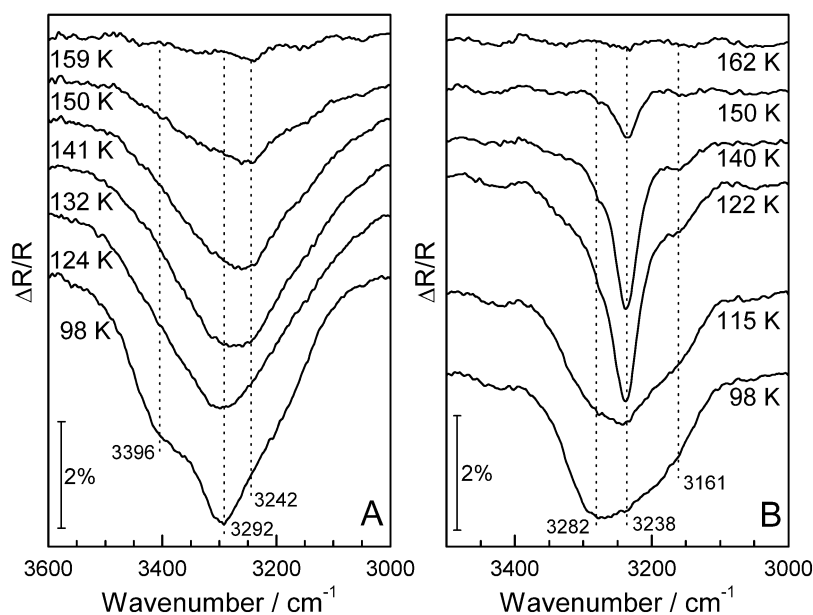


Fig. 8 RAIR spectra of the $\nu(\text{O-H})$ stretching region from 3600 to 3000 cm^{-1} , following the sequential heating of 300 L $\text{C}_2\text{H}_5\text{OH}$ deposited onto (A) a 50 L H_2O film adsorbed on HOPG and (B) a bare HOPG surface. The annealing temperatures are shown in the figure.

be attributed to thermally induced mixing between the C₂H₅OH overlayer and the underlying H₂O film, in agreement with the TPD data. The extent of the mixing cannot be determined by RAIRS alone. However, the TPD data presented earlier shows that mixing between the two layers is extensive enough to disrupt the crystallization of the C₂H₅OH overlayers as seen in the RAIRS.

The downshift in frequency of the $\nu(\text{OH})$ band observed during annealing is characteristic of the formation of hydrogen bonds and suggests an interaction between the C₂H₅OH and H₂O layers that is not present during adsorption at 98 K. The interaction between the C₂H₅OH and H₂O could be a consequence of the formation of a type II clathrate hydrate, which has been previously reported in a Raman study of vapour deposition of C₂H₅OH:H₂O mixtures at 88 K⁶⁸ and for CH₃OH/H₂O mixtures.⁶⁹ However this is not conclusive, since clathrates are usually formed under high pressure conditions. It is more likely that annealing leads to the formation of C₂H₅OH:H₂O hydrogen bonded networks or C₂H₅OH:H₂O clusters,⁶⁸ formed *via* the mutual diffusion of the ices beyond their respective glass transition temperatures. Certainly, the exact nature of the association between the C₂H₅OH and H₂O layers requires further structural analysis to accurately identify the bonding species.

Conclusions

Recent studies have shown that the thermal desorption of interstellar ices is not an instantaneous process as previously thought.¹³ Hence, a better understanding of the thermal desorption of astrophysically relevant molecules adsorbed on dust grains is essential for the accurate modelling of star forming processes. Therefore a detailed RAIRS and TPD investigation of C₂H₅OH adsorption and desorption from model interstellar ices has been performed for the first time. Unlike many other molecules that are detected within interstellar ices, C₂H₅OH has a comparable sublimation temperature to H₂O, and hence gives rise to complex thermal desorption. To fully understand the complicated nature of the desorption processes, three different ice configurations have been studied, including binary layered ice systems consisting of C₂H₅OH adsorbed on top of pre-existing ASW films, layered systems where the deposition order is reversed, and intimate mixtures of C₂H₅OH:H₂O ices. This study shows for the first time that H₂O desorption from a model dust grain can be affected by the presence of a complex organic molecule, such as C₂H₅OH.

Both RAIRS and TPD data show that C₂H₅OH films are incorporated into the underlying H₂O ice during the heating process. This is attributed to a morphology change in the C₂H₅OH ice, where it behaves like a viscous super-cooled fluid. As a result, C₂H₅OH co-desorbs with all three phases of the H₂O-ice: amorphous, crystalline and hexagonal ice. In the case of the thicker underlying H₂O ices, trapped C₂H₅OH molecules desorb during the ASW-CI phase transition *via* a molecular volcano mechanism. Similar C₂H₅OH co-desorption channels are also observed when reversing the deposition sequence, with H₂O adsorbed on top of C₂H₅OH ices of varying thickness. A direct comparison of the C₂H₅OH TPD

from the binary ices with C₂H₅OH TPD recorded from co-deposited C₂H₅OH:H₂O mixtures provides evidence to support thermally induced mixing between the layers. However, the exact nature of the interaction between the two ice films is not fully understood. The thermally induced mixing between C₂H₅OH and ASW ices shows that C₂H₅OH exhibits atypical behaviour when compared to numerous other volatiles detected within astrophysical ices. It exhibits complete co-desorption when deposited beneath ASW and when deposited as a mixture. Furthermore, C₂H₅OH is shown to modify the desorption of the H₂O ice at the ASW-CI phase transition. Such observations have not been previously reported for other astronomically relevant species, deposited either as a binary ice or co-deposited as a mixture. These findings suggest that C₂H₅OH can only be released into the gas-phase in the hotter regions of the ISM (>150 K) when the H₂O itself desorbs. This is consistent with observations of relatively high gas-phase abundances of C₂H₅OH in the vicinity of hot cores. This is in contrast to dark clouds (20 K), where gas-phase C₂H₅OH is not observed.⁷⁻⁹ It is thought that the origin of these high gas-phase abundances arises from the evaporation of chemically rich icy mantles, caused by the heat generated by new born stars.

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